

## EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	2	("5051114").PN.	USPAT; EPO; DERWENT	OR	OFF	2007/03/27 18:53
L2	137	membrane and multilayer and composite and nonporous	USPAT; EPO; DERWENT	AND	ON	2007/03/27 18:53
L3	53	2 and casting	USPAT; EPO; DERWENT	AND	ON	2007/03/27 18:54
L4	33	2 and casting and drying	USPAT; EPO; DERWENT	AND	ON	2007/03/27 18:54

**US-PAT-NO:** 6887408  
**DOCUMENT-  
IDENTIFIER:** US 6887408 B2  
**TITLE:** Porous poly(aryl ether ketone) membranes, processes for their preparation and use thereof  
  
**DATE-ISSUED:** May 3, 2005

**INVENTOR-INFORMATION:**

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**APPL-NO:** 10/836043

**DATE FILED:** April 30, 2004

**PARENT-CASE:**

**CROSS-REFERENCE TO RELATED APPLICATIONS**

This application claims the benefit of, under 35 U.S.C. .sctn.119(e), U.S. Provisional Patent Application No. 60/468,013, filed May 5, 2003.

**INT-CL-ISSUED:** [07] B01D071/06

**INT-CL-CURRENT:**

<b>TYPE</b>	<b>IPC DATE</b>
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CIPS	<u>B01 D 71/06</u> 20060101
CIPS	<u>B01 D 61/00</u> 20060101
CIPS	<u>B01 D 71/00</u> 20060101
CIPS	<u>B32 B 3/26</u> 20060101

**US-CL-ISSUED:** 264/49 , 264/514 , 264/561 , 264/562 , 264/567 , 264/177.18 , 264/346 , 210/500.22 , 210/500.23 , 210/500.27 , 210/500.39 , 528/310 , 521/64

**US-CL-CURRENT:** 264/49 , 210/500.22 , 210/500.23 , 210/500.27 , 210/500.39 , 264/177.18 , 264/346 , 264/514 , 264/561 , 264/562 , 264/567 , 521/64 , 528/310

**FIELD-OF-CLASSIFICATION-SEARCH:** 264/41; 264/45.9 ; 264/49 ; 264/514 ; 264/151 ; 264/557 ; 264/561 ; 264/562 ; 264/567 ; 264/46.3 ; 264/346 ; 264/288.8 ; 264/289.3 ; 264/177.18 ; 264/209.5 ; 210/500.22 ; 210/500.23 ; 210/500.27 ; 210/500.39 ; 528/310 ; 521/62 ; 521/64

**\*\*See application file for complete search history\*\***

## **REF-CITED:**

### **U.S. PATENT DOCUMENTS**

PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL		
<u>4721732</u>	January 1988	Dubrow et al.	521/62	N/A	N/A
<u>4957817</u>	September 1990	Chau et al.	428/436	N/A	N/A
<u>4992485</u>	February 1991	Koo et al.	521/180	N/A	N/A
<u>5064580</u>	November 1991	Beck et al.	264/28	N/A	N/A
<u>5089192</u>	February 1992	Costa	264/49	N/A	N/A
<u>5200078</u>	April 1993	Beck et al.	210/500.23	N/A	N/A
<u>5205968</u>	April 1993	Damrow et al.	264/28	N/A	N/A
<u>5227101</u>	July 1993	Mahoney et al.	264/28	N/A	N/A
<u>5651931</u>	July 1997	Bailey et al.	264/126	N/A	N/A
<u>5997741</u>	December 1999	Shimoda et al.	210/500.27	N/A	N/A
<u>6017455</u>	January 2000	Shimoda et al.	210/500.23	N/A	N/A

## FOREIGN PATENT DOCUMENTS

### FOREIGN-PAT-NO PUBN-DATE COUNTRY US-CL

0 737 506 October 1996 EP

**OTHER PUBLICATIONS** Mark. F. Sonnenschein, Hollow Fiber Microfiltration **Membranes** from Poly(ether ether ketone) (PEEK), Journal of Applied Polymer Science. vol. 72. pp. 175-181, 1999.

Rakeshh. Mehta, et al., Microporour **membranes** based on poly (ether ether ketone) via thermally-induced phase separation, Journal of **Membrane** Science 107 (1195) pp. 95-106, 1995 Elsevier Science B.V.

Matsumoto Yasuyo; others:04, Porus Polyetheretherketone Film and its Preparation, Dec. 4, 1991, pp. 1□315.

Yong Ding et al., Novel Macro and Meso Porous Material Prepared from Miscible Polysulfone/Polyimide Blends,2003 Materials Prepared from Miscible Polysulfone/Poly, Mat.Res.Soc.Symp.Proc.vol. 752 c 2003 Materials Research Society , pp. 8-15.

**ART-UNIT:** 1723

**PRIMARY-EXAMINER:** Mills; Gregory

**ASSISTANT-EXAMINER:** Menon; K S

**ATTY-AGENT-FIRM:** St. Onge Steward Johnston & Reens LLC

## ABSTRACT:

Porous poly(aryl ether ketone) (PAEK) articles are prepared from PAEK/polyimide blends by selective chemical decomposition and subsequent removal of the polyimide phase. Porous PAEK articles exhibit highly interconnected pore structure and a narrow pore size distribution. The porous PAEK articles of the present invention can be utilized

as a porous media for a broad range of applications, including membranes for fluid separations, such as microfiltration, ultrafiltration, nanofiltration, and as a sorption media.

30 Claims, 3 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 3

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**Abstract Text - ABTX (1):**

Porous poly(aryl ether ketone) (PAEK) articles are prepared from PAEK/polyimide blends by selective chemical decomposition and subsequent removal of the polyimide phase. Porous PAEK articles exhibit highly interconnected pore structure and a narrow pore size distribution. The porous PAEK articles of the present invention can be utilized as a porous media for a broad range of applications, including membranes for fluid separations, such as microfiltration, ultrafiltration, nanofiltration, and as a sorption media.

**TITLE - TI (1):**

Porous poly(aryl ether ketone) membranes, processes for their preparation and use thereof

**Brief Summary Text - BSTX (2):**

The present invention relates to a process for the preparation of porous articles of poly(aryl ether ketone) (herein after referred to as PAEK). More particularly, the present invention relates to preparation of porous PAEK articles from PAEK/polyimide blends by a melt extrusion process followed by the removal of the polyimide phase. Porous PAEK articles exhibit uniform pore size distribution and can be used as a porous media for a broad range of applications, including porous membranes for fluid separations, such as microfiltration, nanofiltration, and ultrafiltration, and as a sorption media.

**Brief Summary Text - BSTX (4):**

Microporous polymeric membranes are well known in the art and are used widely for filtration and purification processes, such as filtration of waste water, preparation of ultrapure water and in medical, pharmaceutical or food applications, including removal of microorganisms, dialyses and protein filtration. While these membranes have found

broad utility for a variety of purposes, they suffer from several disadvantages, such as broad and frequently non uniform pore size distribution, and limited chemical, solvent and thermal resistance.

#### **Brief Summary Text - BSTX (5):**

Poly(aryl ether ketone)s represent a class of semi-crystalline engineering thermal plastics with outstanding thermal properties and chemical resistance. One of the representative polymers in this class is poly(ether ether ketone), PEEK, which has a reported continuous service temperature of approximately 250.degree. C. PAEK polymers are virtually insoluble in all common solvents at room temperature. These properties make PAEK attractive materials for porous membrane preparation. However, the application of PAEK polymers in membrane fabrication has been limited owing to their intractability, which prevents the use of conventional solvent-based methods of membrane casting.

#### **Brief Summary Text - BSTX (6):**

It is known in the art to prepare porous PEEK membranes from solutions of strong acids, such as concentrated sulfuric acid. PEEK can undergo sulfonation in the concentrated sulfuric acid media and thus lose some of its desirable sought after properties. U.S. Pat. No. 6,017,455 discloses preparation of non-sulfonated porous PEEK membranes from concentrated sulfuric acid solvents sufficiently diluted by water to prevent sulfonation. The membranes are formed by casting PEEK solution to form a film followed by coagulation in a concentrated sulfuric acid. This membrane preparation process is highly complicated and produces large amounts of waste acid.

#### **Brief Summary Text - BSTX (7):**

U.S. Pat. No. 5,997,741 discloses preparation of porous PEEK membranes by forming a solution of PEEK polymer in a concentrated sulfuric acid at the temperature of 15.degree. C. or lower to prevent sulfonation. The solution is processed and cast at a subambient temperature, followed by coagulation in water or in a concentrated sulfuric acid. Only dilute PEEK solutions can be formed in the concentrated sulfuric acid which adversely affects film forming characteristics, the mechanical characteristics, and the pore morphology of the porous PEEK membranes.

#### **Brief Summary Text - BSTX (8):**

U.S. Pat. Nos. 4,992,485 and 5,089,192 disclose preparation of PEEK membranes from non-sulfonating acid solvents that include methane sulfonic acid and trifluoromethane sulfonic acid. European Patent Specification EP 0737506 discloses preparation of improved polymeric membranes based on PEEK admixtures with

polyethylene terephthalate. The membranes are formed by the solution casting process from a methane sulfuric acid/sulfuric acid solvent mixture.

**Brief Summary Text - BSTX (9):**

The acid based solvent systems for manufacturing of porous PEEK membranes disclosed in the art are highly corrosive, frequently toxic and generate substantial environmental and disposal problems. For these and other reasons, the acid based casting processes have found limited commercial use.

**Brief Summary Text - BSTX (10):**

An alternative to the acid based solvent system for PEEK membrane preparation involves the use of high boiling point solvents and plasticizers that dissolve PEEK polymer at elevated temperatures. U.S. Pat. Nos. 4,957,817 and 5,064,580, both issued to Dow Chemical Co., disclose preparation of porous PEEK articles from its admixture with organic polar solvents having a boiling point in the range of 191.degree. C. to 380.degree. C., such as benzophenone and 1-chloronaphthalene, and organic plasticizers capable of dissolving at least 10 weight percent of PEEK, respectively. The final porous article is formed by removing the organic polar solvents and/or plasticizers by dissolution into a low boiling temperature solvent.

**Brief Summary Text - BSTX (11):**

U.S. Pat. No. 5,200,078 discloses preparation of microporous PEEK membranes from its mixtures with plasticizers wherein the membrane undergoes a drawing step prior to or after the plasticizer is removed by leaching.

**Brief Summary Text - BSTX (12):**

U.S. Pat. No. 5,227,101 issued to Dow Chemical Co. discloses preparation of microporous membranes from poly(aryl ether ketone) type polymer by forming a mixture of an unsulfonated PEEK type polymer, a low melting point crystallizable polymer, and a plasticizer, heating the resulting mixture, extruding or casting the mixture into a membrane, quenching or coagulating the membrane and leaching the pore forming components.

**Brief Summary Text - BSTX (13):**

U.S. Pat. No. 5,205,968, issued to Dow Chemical Co., discloses preparation of microporous membranes from a blend containing a poly(aryl ether ketone) type polymer, an amorphous polymer and a solvent.

### **Brief Summary Text - BSTX (14):**

M. F. Sonnenschein in the article entitled "Hollow fiber microfiltration **membranes** from poly(ether ether ketone)", published in the Journal of Applied Polymer Science, Volume 72, pages 175-181, 1999, describes preparation of PEEK hollow fiber **membranes** by thermal phase inversion process. The use of a leachable additive polymer, such as polysulfone, is proposed to enhance **membrane** performance.

### **Brief Summary Text - BSTX (15):**

It is also known in the art to prepare porous PEEK **membranes** from its blends with a compatible poly(ether imide) polymer, PEI. Preparation of such **membranes** is described by R. S. Dubrow and M. F. Froix in U.S. Pat. No. 4,721,732 and by R. H. Mehta et al. in an article entitled "Microporous **membranes** based on poly(ether ether ketone) via thermally induced phase separation", published in the Journal of **Membrane** Science, Volume 107, pages 93-106, 1995. The porous structure of these PEEK **membranes** is formed by leaching the poly(ether imide) component with an appropriate strong solvent such as dimethylformamide. However, as described by Mehta et al., the quantitative removal of PEI component by leaching is essentially impossible (i.e., Mehta et al. are unable to achieve substantially complete removal of PEI) which in turn can lead to an inferior **membrane** performance.

### **Brief Summary Text - BSTX (16):**

Japan Kokai Tokkyo Koho 91273038 assigned to Sumitomo Electric Industries, Ltd., discloses preparation of porous PEEK **membranes** by an ion track etching method.

### **Brief Summary Text - BSTX (18):**

M. L. Bailey et al. in U.S. Pat. No. 5,651,931 describe a sintering process for the preparation of biocompatible filters, including PEEK filters. The filters are formed from a PEEK powder of a preselected average particle size by first pressing the powder into a "cake" followed by sintering in an oven or furnace. The process is limited to preparation of filters with a relatively large pore size and a broad pore size distribution and does not provide an economic means of forming large **membrane** area fluid separation devices.

### **Brief Summary Text - BSTX (20):**

Thus there still remains a need in the art to produce porous PAEK articles, including porous **membranes** with improved properties, by a simple and commercially scalable process that is environmentally benign and does not utilize corrosive or toxic chemicals in **membrane** fabrication.

### **Brief Summary Text - BSTX (22):**

It is thus an objective of this invention to provide a simple, cost effective, and industrially feasible process for the preparation of porous PAEK articles and in particular PAEK membranes.

### **Brief Summary Text - BSTX (24):**

A further objective of this invention is to provide an improved fluid separation process that utilizes solvent and heat resistant PAEK membranes.

### **Brief Summary Text - BSTX (26):**

According to one embodiment of the present invention, the above objectives and other objectives that are apparent to those skilled in the art are achieved by a process of the preparation of a porous poly(aryl ether ketone) article comprising: a. forming a blend of poly(aryl ether ketone) type polymer with a polyimide; b. forming a shaped article from the blend by extrusion, casting or molding; c. decomposing the polyimide in the shaped article into low molecular weight fragments by chemical means; and d. removing the low molecular weight fragments from the article.

### **Brief Summary Text - BSTX (28):**

According to another embodiment of the present invention, the above objectives and other objectives that are apparent to those skilled in the art are achieved by a method for separating a fluid mixture into a fraction enriched in a first component and a fraction depleted in the first component, comprising the step of contacting said fluid mixture with a fluid separation membrane, the membrane having been formed by a process including the steps of: a. forming a blend of poly(aryl ether ketone) type polymer with a polyimide; b. forming a shaped article from said blend by extrusion, casting or molding; c. decomposing said polyimide in said shaped article into low molecular weight fragments by chemical means; d. removing said low molecular weight fragments from said article,

### **Brief Summary Text - BSTX (29):**

whereby said fraction enriched in the first component and said fraction depleted in the first component are generated by preferentially permeating a portion of said fluid mixture through said fluid separation membrane.

### **Drawing Description Text - DRTX (3):**

FIG. 2 is the Scanning Electron Microscopy photomicrograph of the cross-section of the porous poly(ether ether ketone) membrane of present invention prepared from the poly(ether ether ketone)/poly(ether imide) blend (50/50, by weight) at a magnification of 10,000.times.showing the uniform and highly interconnected porous structure.

#### Drawing Description Text - DRTX (4):

FIG. 3 is the Scanning Electron Microscopy photomicrograph of the cross-section of the porous poly(ether ether ketone) membrane of present invention prepared from the poly(ether ether ketone)/poly(ether imide) blend (30/70, by weight) at a magnification of 10,000.times.showing interconnected worm-like porous structure.

#### Detailed Description Text - DETX (2):

The porous articles of this invention are comprised of poly(aryl ether ketone)s. These articles are prepared from a blend of a poly(aryl ether ketone) type polymer with a compatible polyimide. First a precursor article is formed from the poly(aryl ether ketone)/polyimide blend by extrusion, casting or molding followed by a selective chemical decomposition of the polyimide phase to form the final porous article.

#### Detailed Description Text - DETX (28):

The poly(aryl ether ketone)/polyimide precursor blends can be fabricated into a flat sheet film, a fiber, a hollow fiber or other desired shape article by a melt extrusion, a casting or a molding process. The article configuration will depend on the intended use. The article can be optionally annealed at a temperature between 150 to 350.degree. C., preferably between 200 to 300.degree. C. to increase the crystallinity prior to the removal of the polyimide phase.

#### Detailed Description Text - DETX (30):

In some embodiments, it is desirable to perform the final drying step from a low surface tension solvent, such a hydrocarbon, or a fluorocarbon. It is known in the art that drying a porous article from such low surface tension solvent can preserve the porous structure. Preferred hydrocarbons include pentane, hexane, cyclohexane heptane, octane, and mixtures thereof. Preferred fluorocarbon solvents include chlorofluorocarbons, for example, Freon 113.RTM. chlorofluorocarbon, and perfluorocarbons, for example, Fluorinert 75.RTM.. The porous articles can be dried in air or in an inert gas such as nitrogen. Drying may be also carried out under vacuum. The articles may be dried at temperatures at which drying takes place at a reasonable rate and which do not adversely affect the porous structure. The drying temperatures can be between about 0.degree. C. and about 200.degree. C., preferably between 40.degree. C. and 100.degree. C. The drying time can be as short as about 30 seconds in a continuous drying operation and as

long as 24 hours or longer in an enclosed oven. The thus formed porous articles can also be optionally annealed at a temperature between 150 and 350.degree. C., preferably between 200 to 300.degree. C. to increase the crystallinity. In some embodiments, the annealing can be carried out by immersing the porous poly(aryl ether ketone) article into a liquid media, such as glycerin maintained at a desired elevated temperature. This annealing step can be carried out in lieu or in addition to the annealing of the poly(aryl ether ketone)/polyimide blend article prior to leaching.

#### **Detailed Description Text - DETX (33):**

In some embodiments of this invention, it is desirable to draw the poly(aryl ether ketone) article to affect the shape and the size of pores and to improve mechanic properties. The membrane articles are drawn to improve permeability, separation efficiency or mechanical properties. The drawing can be performed on the poly(aryl ether ketone)/polyimide blend precursor prior to the removal of the polyimide phase or on the porous poly(aryl ether ketone) article after the polyimide phase has been decomposed and removed, or both. Further more, the drawing step can be carried out prior or after the drying step. In some embodiments, the porous structure can be impregnated with a liquid processing aid, such as glycerin, prior to drawing. The articles are drawn by stretching the films, the fiber, or the hollow fiber under tension. Conventional equipments, such as godets, are utilized to draw the articles. The articles are drawn to a ratio of between 1.1 to about 10 or more. The draw ratio is defined as the ratio of the final length after drawing to the original length before drawing:  $L_{\text{sub},f}/L_{\text{sub},i}$ , where  $L_{\text{sub},f}$  is the final length after drawing and  $L_{\text{sub},i}$  is the initial length before drawing.

#### **Detailed Description Text - DETX (36):**

The porous articles of this invention can be in the form of a flat sheet film, a fiber, a tube, a hollow fiber, or any other desirable shape. The porous articles of this invention can be used as an adsorption media, as a separator in a device, such as a battery separator, or as a fluid separation membrane. The membrane articles can be in the form of a flat sheet, in a tubular form, or a hollow fiber configuration. In the case of hollow fibers, the fiber preferably possess an outside diameter from about 50 to about 5,000 micrometers, more preferably from about 80 to about 1,000 micrometers, with a wall thickness from about 10 to about 1,000 micrometers, preferably from 20 to 500 micrometers. In the case of films, the film preferably possess a thickness of from about 10 to about 1,000 micrometers, most preferably from about 25 to about 500 micrometers. The films may be optionally supported by a permeable cloth or a screen.

#### **Detailed Description Text - DETX (37):**

The porous poly(aryl ether ketone) membranes of this invention can be used directly for a number of fluid separation processes, such as microfiltration, ultrafiltration, nano-

filtration and gas separation. The fluid separation method typically involves contacting a feed fluid with the poly(aryl ether ketone) membrane of this invention under conditions that sustain a pressure differential across the PEAK membrane. At least a fraction of the feed mixture permeates through the PEAK membrane. In the process of permeation the permeate fraction of the feed mixture is depleted in a component and the non-permeate fraction of the feed mixture is enriched in this component. The component or components can be in the form of a solute dissolved in the feed fluid, a solid matter suspended in the feed fluid, or a gaseous component being a part of the feed gas mixture. Further more, the fluid separation method can be a cross flow filtration process or a dead-end filtration process.

#### **Detailed Description Text - DETX (38):**

The porous poly(aryl ether ketone)s can be further used as substrates in preparation of composite fluid separation membranes. Such composite membranes consist of a porous or a nonporous separation layer superimposed or formed directly on the porous poly(aryl ether ketone) substrate. The separation layer can be formed by a direct casting process, by an interfacial polymerization process or other processes well known in the art.

#### **Detailed Description Text - DETX (39):**

It is also within the scope of present invention to form multilayer porous PAEK articles or PAEK articles with multiple porous zones. The multizone porous articles that contain porous zones that differ at least by about 10% in the average pore size or by at least about 5% in the pore volume are known to impart certain advantages to material mechanical or separation characteristics. For example, the multizone porous membranes are known to provide improved mechanical properties particularly in fluid separation applications that require periodic back washing, to exhibit a lower cross membrane pressure drop, a decreased susceptibility to breach in membrane separation layer and a decreased propensity to fouling. The multizone porous articles are formed from two or more PAEK/polyimide blends that differ in blend chemical composition. The blends can contain different PAEK and polyimide polymer components. Preferably, the chemical composition of individual blends differs in the PAEK/polyimide ratio. The PAEK polymers content of the first blend can differ from the PAEK polymer content of the second and any additional blend by at least 1 weight percent, preferably by at lease 5 weight percent, more preferably by at least 10 weight percent.

#### **Detailed Description Text - DETX (40):**

The multilayer flat sheet PAEK articles or multilayer PAEK articles of the tubular configuration can contain two, three or more contiguous layers that differ in the average pore size and/or pore volume. Furthermore, the individual layer can vary from about 1%

of the overall article thickness or less to about 99% of the article thickness or more, typically from 10% to 90% of the article thickness. The layer comprised of the smaller average size pores can be about 1 micrometer thick or less to about 100 micrometers thick or more and is supported by or sandwiched between layers with a substantially larger average pore size.

#### Detailed Description Text - DETX (45):

A porous PEEK membrane was obtained by treating the PEEK/PEI film in monoethanolamine maintained at 80.degree. C. for 8 hours. The film became opaque after the PEI component was removed. The porous film was then washed with methanol, and dried under vacuum at 50.degree. C. overnight. The thickness of the porous film was 78 micrometers. The weight loss of the PEEK/PEI blend film was 50%, indicating that the PEI phase had been quantitatively removed. ATR-FTIR spectra confirmed the quantitative removal of the PEI component (FIG. 1). The 1720 cm.sup.-1 peak assigned to C.dbd.O group in the imide linkage is completely absent from the FT-IR spectrum of the porous PEEK film. The SEM microphotograph of the PEEK membrane cross section is shown in FIG. 2. The microphotograph indicates that the membrane is highly porous and possesses a uniform pore size distribution. The pores are worm-like and interconnected. The gas transport properties of the porous PEEK membrane are summarized in Table 1. The ideal gas separation factor for the gas pair of O.sub.2 and N.sub.2 was determined to be 0.97 and the ideal gas separation factor for the gas pair of He and N.sub.2 was determined to be 2.5.

#### Detailed Description Text - DETX (49):

A porous PEEK membrane was obtained by treating the PEEK/PEI film with the monoethanolamine maintained at 80.degree. C. for 8 hours. The film became opaque after the PEI component was removed. The porous film was then washed with methanol, and dried under vacuum at 50.degree. C. overnight. The thickness of the porous film was 78 micrometers. The weight loss of the PEEK/PEI blend film was 70%, indicating that the PEI phase had been quantitatively removed. The SEM microphotograph of the PEEK film cross section is shown in FIG. 3. The microphotograph indicates that the membrane is highly porous. The pores are worm-like and interconnected.

#### Detailed Description Paragraph Table - DETL (1):

TABLE 1 Gas transport properties of porous PEEK membrane Pure gas Permeance (GPU)\* O.sub.2 7150 N.sub.2 7380 He 18500 \*1 GPU = 1 .times. 10.sup.-6 cm.sup.3 (STP)/cm.sup.2 .multidot. s .multidot. cmHg.

#### Claims Text - CLTX (1):

1. A process for the preparation of a porous poly(aryl ether ketone) article comprising the steps of: a. forming a blend of poly(aryl ether ketone) polymer with a polyimide, b. forming a shaped article from said blend by extrusion, casting or molding, c. decomposing said polyimide in said shaped article into low molecular weight fragments by chemical means by contacting the shaped article with ammonia, tetraalkylammonium hydroxide, primary aliphatic amine, secondary aliphatic amine, or a mixture thereof, d. removing said low molecular weight fragments from said article.

**Claims Text - CLTX (4):**

4. The process of claim 1 further comprising drying the porous article under conditions that substantially preserves the porous structure.

**Claims Text - CLTX (5):**

5. The process of claim 4 wherein said drying process is carried out from a hydrocarbon or a fluorocarbon solvent.

**Claims Text - CLTX (21):**

21. The process of claim 15 wherein said flat sheet, said tube, or said hollow fiber is a fluid separation membrane.

**Claims Text - CLTX (23):**

23. The process of claim 1 wherein said shaped poly(aryl ether ketone) article is a multilayer article formed from two or more poly(aryl ether ketone) polymer polyimide blends that differ in blend chemical composition.

**Other Reference Publication - OREF (1):**

Mark. F. Sonnenschein, Hollow Fiber Microfiltration Membranes from Poly(ether ether ketone) (PEEK), Journal of Applied Polymer Science. vol. 72. pp. 175-181, 1999.

**Other Reference Publication - OREF (2):**

Rakeshh. Mehta, et al., Microporour membranes based on poly (ether ether ketone) via thermally-induced phase separation, Journal of Membrane Science 107 (1195) pp. 95-106, 1995 Elsevier Science B.V.

**US-PAT-NO:** 5085676  
**DOCUMENT-IDENTIFIER:** US 5085676 A  
\*\*See image for Certificate of Correction\*\*  
**TITLE:** Novel multicomponent fluid separation membranes  
  
**DATE-ISSUED:** February 4, 1992

**INVENTOR-INFORMATION:**

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Hayes; Richard A.	Parkersburg	WV	N/A	N/A
Manos; Phillip	Wilmington	DE	N/A	N/A

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E. I. du Pont de Nemours and Company	Wilmington	DE	N/A	N/A	02

**APPL-NO:** 07/622419

**DATE FILED:** December 4, 1990

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<b>TYPE</b>	<b>IPC DATE</b>
CIPS	<u>C08 L 77/00</u> 20060101
CIPS	<u>B01 D 71/56</u> 20060101

CIPS	<u>B01 D 69/12</u>	20060101
CIPS	<u>B01 D 69/00</u>	20060101
CIPS	<u>B01 D 69/08</u>	20060101
CIPS	<u>B01 D 71/00</u>	20060101
CIPS	<u>B01 D 71/64</u>	20060101

**US-CL-ISSUED:** 55/158 , 55/16 , 210/500.23 , 210/50039.500.41 ,  
264/41

**US-CL-CURRENT:** 96/13, 210/500.23 , 210/500.39 , 210/500.41 , 264/41 ,  
96/10

**FIELD-OF-CLASSIFICATION-SEARCH:** 55/16; 55/68 ; 55/158 ; 264/41 ; 210/500.23 ;  
210/500.37 ; 210/500.38 ; 210/500.39 ; 210/500.41

**\*\*See application file for complete search history\*\***

#### **REF-CITED:**

#### **U.S. PATENT DOCUMENTS**

#### **PAT-NO ISSUE-DATE PATENTEE-NAME US-CL**

<u>2947687</u>	August 1960	Lee	210/23	N/A	N/A
<u>2953502</u>	September 1960	Binning et al.	202/42	N/A	N/A
<u>2960462</u>	November 1960	Lee et al.	208/308	N/A	N/A
<u>2966235</u>	December 1960	Kammermeyer	183/115	N/A	N/A
<u>2970106</u>	January 1961	Binning et al.	208/347	N/A	N/A
<u>3172741</u>	March 1965	Jolley	55/16	N/A	N/A
<u>3508994</u>	April 1970	Nyrop	156/280	N/A	N/A
<u>3616607</u>	November 1971	Klass et al.	55/16	N/A	N/A
<u>3648845</u>	March 1972	Riley	210/490	N/A	N/A
<u>3657113</u>	April 1972	Stancell et al.	210/23	N/A	N/A
<u>4071590</u>	January 1978	Strathmann	N/A	264/41	N/A
<u>4086310</u>	April 1978	Bottenbruch et al.	264/41	N/A	N/A
<u>4113628</u>	September 1978	Alegranti	210/500	N/A	N/A
<u>4132824</u>	January 1979	Kimura et al.	428/220	N/A	N/A

<u>4155793</u>	May 1979	Salemme et al.	156/246	N/A	N/A
<u>4156597</u>	May 1979	Browall	55/16	N/A	N/A
<u>4164437</u>	August 1979	Henne et al.	N/A	264/41	N/A
<u>4192842</u>	March 1980	Kimura et al.	264/298	N/A	N/A
<u>4260652</u>	April 1981	Taketani et al.	427/245	N/A	N/A
<u>4378324</u>	March 1983	Makino et al.	264/41	N/A	N/A
<u>4440643</u>	April 1984	Makino et al.	210/500.2	N/A	N/A
<u>4460526</u>	July 1984	Makino et al.	264/41	N/A	N/A
<u>4474662</u>	October 1984	Makino et al.	210/500.2	N/A	N/A
<u>4474858</u>	October 1984	Makino et al.	428/473.5	N/A	N/A
<u>4485056</u>	November 1984	Makino et al.	264/41	N/A	N/A
<u>4512893</u>	April 1985	Makino et al.	210/500.2	N/A	N/A
<u>4528004</u>	July 1985	Makino et al.	55/158	N/A	N/A
<u>4529646</u>	July 1985	Sundet	N/A	264/41	N/A
<u>4602922</u>	July 1986	Cabasso et al.	55/158	N/A	N/A
<u>4664669</u>	May 1987	Ohyabu et al.	623/66	N/A	N/A
<u>4689267</u>	August 1987	Takamizawa et al.	428/376	N/A	N/A
<u>4713292</u>	December 1987	Takemura et al.	428/373	N/A	N/A
<u>4714481</u>	December 1987	Matsuura et al.	55/158	N/A	N/A
<u>4717394</u>	May 1988	Hayes	55/16	N/A	N/A
<u>4741829</u>	May 1988	Takemura et al.	210/500.23	N/A	N/A
<u>4756932</u>	July 1988	Puri	427/175	N/A	N/A
<u>4772392</u>	September 1988	Sanders, Jr. et al.	N/A	264/41	N/A
<u>4826599</u>	May 1989	Bikson et al.	210/500.3	N/A	N/A
<u>4938902</u>	July 1990	Nakamura et al.	N/A	264/41	N/A
<u>4955993</u>	September 1990	Sanders, Jr. et al.	N/A	264/41	N/A
<u>4975228</u>	December 1990	Sanders, Jr. et al.	264/41	N/A	N/A
<u>4980063</u>	December 1990	Mahoney et al.	N/A	264/41	N/A
<u>5009824</u>	April 1991	Walch et al.	N/A	264/41	N/A
<u>5011637</u>	April 1991	Overman, III et al.	264/41	N/A	N/A

## **FOREIGN PATENT DOCUMENTS**

**FOREIGN-PAT-NO PUBN-DATE COUNTRY US-CL**

62-253785      April 1989      JP

**ART-UNIT:**                  135

**PRIMARY-EXAMINER:** Spitzer; Robert

### **ABSTRACT:**

A process for preparing multicomponent gas separation membranes is disclosed. The process involves casting two or more solutions of polymer, and partially removing solvent from the side of the cast polymer that is to form the gas separation layer of the membrane. The membrane is then quenched to freeze its structure and then the remainder of the solvent removed to form the gas separation membrane.

78 Claims, 0 Drawing figures

Exemplary Claim Number: 1

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### **Abstract Text - ABTX (1):**

A process for preparing multicomponent gas separation membranes is disclosed. The process involves casting two or more solutions of polymer, and partially removing solvent from the side of the cast polymer that is to form the gas separation layer of the membrane. The membrane is then quenched to freeze its structure and then the remainder of the solvent removed to form the gas separation membrane.

### **TITLE - TI (1):**

Novel multicomponent fluid separation membranes

### **Brief Summary Text - BSTX (2):**

The present invention relates to fabrication of composite gas separation membranes.

### **Brief Summary Text - BSTX (4):**

The separation of one or more gases from a complex multicomponent mixture of gases is necessary in a large number of industries. Such separations currently are undertaken commercially by processes such as cryogenics, pressure swing adsorption and **membrane** separations. In certain types of gas separations, **membrane** separations have been found to be economically more viable than other processes.

#### **Brief Summary Text - BSTX (5):**

In a pressure driven gas **membrane** separation process, one side of the gas separation **membrane** is contacted with a complex multicomponent gas mixture and certain of the gases of the mixture permeate through the **membrane** faster than the other gases. Gas separation **membranes** thereby allow some gases to permeate through them while serving as a barrier to other gases in a relative sense. The relative gas permeation rate through the **membrane** is a property of the **membrane** material composition. It has been suggested in the prior art that the intrinsic **membrane** material selectivity is a combination of gas diffusion through the **membrane**, controlled in part by the packing and molecular free volume of the material, and gas solubility within the material. It is highly desirable to form defect free dense separating layers in order to retain high gas selectivity.

#### **Brief Summary Text - BSTX (6):**

The preparation of commercially viable gas separation **membranes** has been greatly simplified with asymmetric **membranes**. Asymmetric **membranes** are prepared by the precipitation of polymer solutions in solvent-miscible nonsolvents. Such **membranes** are typified by a dense separating layer supported on an anisotropic substrate of a graded porosity and are generally prepared in one step. Examples of such **membranes** and their methods of manufacture are shown in U.S. Pat. Nos. 4,113,628; 4,378,324; 4,460,526; 4,474,662; 4,485,056; and 4,512,893. U.S. Pat. No. 4,717,394 shows preparation of asymmetric separation **membranes** from selected polyimides.

#### **Brief Summary Text - BSTX (7):**

A shortcoming of asymmetric gas separation **membranes** concerns the stability of these **membranes** under end use environmental conditions because asymmetric **membranes** are typically composed of homogeneous materials. That is to say, the dense separating layer and the porous substrate layer of the **membrane** are compositionally the same.

#### **Brief Summary Text - BSTX (8):**

For some gas separations, such as acid gas separations, it has been found advantageous in the prior art to employ separating **membranes** comprising materials which have high

intrinsic acid gas solubility. However, asymmetric membranes prepared from materials with high acid gas solubilities tend to plasticize and undergo compaction under acid gas separation end use conditions. In addition, asymmetric membranes may be plasticized and compacted due to components such as water which may be in the gas mixtures to be separated. As a result, asymmetric gas separation membranes prepared from hydrophilic materials may be adversely affected under such conditions.

#### Brief Summary Text - BSTX (9):

Composite gas separation membranes typically have a dense separating layer on a preformed microporous substrate. The separating layer and the substrate are usually different in composition. Examples of such membranes and their methods of manufacture are shown in U.S. Pat. Nos. 4,664,669; 4,689,267; 4,741,829; 2,947,687; 2,953,502; 3,616,607; 4,714,481; 4,602,922; 2,970,106; 2,960,462; and 4,713,292, as well as in Japanese 63-218213.

#### Brief Summary Text - BSTX (10):

U.S. Pat. No. 4,664,669 discloses hollow fiber composite membranes of a dense, polyorganosilane polymer and an ultra-microporous layer supported on a porous substrate. U.S. Pat. Nos. 4,689,267 and 4,714,481 show hollow fiber composite membranes that include a dense coating of a poly(silylacetylene) on a porous hollow fiber support. U.S. Pat. No. 4,741,829 shows bicomponent, melt-spun hollow fiber membranes. U.S. Pat. No. 4,826,599 shows forming hollow fiber composite membranes by coating a porous hollow fiber substrate with a solution of membrane forming material, and coagulating the membrane forming material. Japanese patent application 63-218,213, published Sept. 12, 1988, shows coextruding two solutions of polysulfone to form a composite membrane. U.S. Pat. No. 2,947,687 shows composite membranes that include a thin layer of ethyl cellulose. U.S. Pat. No. 2,953,502 shows thin, non-porous plastic membranes. U.S. Pat. No. 2,970,106 shows composite membranes that include modified cellulose acetate-butyrate. U.S. Pat. No. 3,616,607 shows dense polyacrylonitrile film onto a nonporous preforms. U.S. Pat. No. 4,602,922 shows a polyorganosiloxane layer between a porous substrate and the dense separation layer of a composite membrane. U.S. Pat. No. 4,713,292 melt-spun, multi-layer composite hollow fiber membranes. U.S. Pat. No. 2,960,462 shows a non-porous selective film laminated onto a thicker, non-porous permeable film.

#### Brief Summary Text - BSTX (11):

Composite gas separation membranes have evolved to a structure of an ultrathin, dense separating layer supported on an anisotropic, microporous substrate. These composite membrane structures can be prepared by laminating a preformed ultrathin dense separating layer on top of a preformed anisotropic support membrane by a

multistep process. Examples of such membranes and their methods of manufacture are shown in U.S. Pat. Nos. 4,689,267; 4,741,829; 2,947,687; 2,953,502; 2,970,106; 4,086,310; 4,132,824; 4,192,824; 4,155,793; and 4,156,597.

#### Brief Summary Text - BSTX (12):

U.S. Pat. No. 4,086,310 shows preparation of composite membranes from supported, ultra-thin, dense polycarbonate. U.S. Pat. Nos. 4,132,824 and 4,192,842 show ultra-thin dense 4-methylpentene film composite membranes. U.S. Pat. No. 4,155,793 shows composite membranes that include an ultra-thin, dense film on a porous substrate. U.S. Pat. No. 4,156,597 shows a composite membrane that includes an ultra-thin, dense polyetherimide separation layer.

#### Brief Summary Text - BSTX (13):

Composite gas separation membranes are generally prepared by multistep fabrication processes. Typically, the preparation of composite gas separation membrane requires first forming an anisotropic, porous substrate. This is followed by contacting the substrate with a membrane-forming solution. Examples of such methods are shown in U.S. Pat. Nos. 4,826,599; 3,648,845; and 3,508,994.

#### Brief Summary Text - BSTX (14):

U.S. 3,508,994 shows contacting a porous substrate with a membrane forming solution. U.S. Pat. No. 3,648,845 shows coating a porous substrate with a buffer layer followed by solution casting a separating layer of cellulose acetate. Dip coating a polymer solution onto the substrate also may be employed. Examples of such methods are shown in U.S. Pat. Nos. 4,260,652; 4,440,643; 4,474,858; 4,528,004; 4,714,481; and 4,756,932. U.S. Pat. No. 4,260,652 dip coats a polymer onto a substrate. U.S. Pat. No. 4,440,643; 4,474,858; and 4,528,004 show composite polyimide membranes formed by coating a substrate. U.S. Pat. No. 4,714,481 dipcoats polyacetylene onto a substrate to form a composite membrane. U.S. Pat. No. 4,756,932 shows forming composite hollow fiber membranes by dip coating.

#### Brief Summary Text - BSTX (15):

The multistep fabrication processes of the prior art tend to be expensive and time consuming. In addition, the composite membranes produced by these multistep processes can experience failure and poor performance due to defects in the substrate and separating layer. A need therefore exists for a membrane and a process of manufacture which avoids the above shortcomings of the prior art membranes and processes.

#### Brief Summary Text - BSTX (17):

The invention provides a multicomponent gas separation **membrane** prepared by novel process of simultaneously coextruding at least two film forming polymer solutions to form a nascent **membrane**, followed by precipitation to form a **composite** multicomponent **membrane** comprised of a dense or asymmetric gas separating layer and a microporous layer which structurally supports the separating layer. The film-forming polymer may be selected from polymers such as polysulfones, polyether sulfones, polyetherimides, polyimides or polyamides. The nascent **membrane** can be optionally partially dried prior to coagulating of the **membrane** in a fluid bath. The nascent **membrane** is quenched and then the remainder of the solvent is removed to form the gas separation **membrane**. The polymer solutions can be coextruded to form a multicomponent **membrane** with either of the polymer solutions forming the separating or support portion of the fiber.

#### Brief Summary Text - BSTX (18):

The multicomponent **membrane** may be formed into hollow fibers as well as shapes such as films. The multicomponent **membranes** have at least two components comprising a first layer material for supporting a second, separating layer for separating gases. The second layer can be in the form of an asymmetric **membrane** which contains a dense gas separating layer on the exterior surface of the **membrane**.

#### Brief Summary Text - BSTX (20):

The present invention allows for ease of manufacture of multicomponent gas separation **membranes**. In manufacture of the **membranes**, a wide range of materials may be used as the gas separating layer. Suitable gas separating layer **membrane** materials may include those found generally useful for asymmetric gas separation **membranes**. These materials include polyamides, polyimides, polyesters, polycarbonates, copolycarbonate esters, polyethers, polyetherketones, polyetherimides, polyethersulfones, polysulfones, polyvinylidene fluoride, polybenzimidazoles, polybenzoxazoles, polyacrylonitrile, cellulosic derivatives, polyazoaromatics, poly(2,6-dimethylphenylene oxide), polyphenylene oxide, polyureas, polyurethanes, polyhydrazides, polyazomethines, polyacetals, cellulose acetates, cellulose nitrates, ethyl cellulose, styrene-acrylonitrile copolymers, brominated poly(xylylene oxide), sulfonated poly(xylylene oxide), tetrahalogen-substituted polycarbonates, tetrahalogen-substituted polyesters, tetrahalogen-substituted polycarbonate esters, polyquinoxaline, polyamideimides, polyamide esters, blends thereof, copolymers thereof, substituted materials thereof, and the like. In addition, suitable gas separating layer **membrane** materials may include those found useful as the dense separating layer of **composite** gas separation **membranes**. These materials include polysiloxanes, polyacetylenes, polyphosphazenes, polyethylenes, poly(4-methylpentene), poly(trimethylsilylpropyne), poly(trialkylsilylacetylenes), polyureas, polyurethanes, blends thereof, copolymers

thereof, substituted materials thereof, and the like. It is further anticipated that polymerizable substances, that is, materials which cure to form a polymer, such as vulcanizable siloxanes and the like, may be suitable gas separating layers for the multicomponent gas separation **membranes** of the present invention. Preferred materials for the dense gas separating layer include aromatic polyamide and aromatic polyimide compositions.

#### **Brief Summary Text - BSTX (24):**

Suitable substrate layer materials for the **membranes** of the present invention may include polysulfone, polyether sulfone, polyamide, polyimide, polyetherimide, polyesters, polycarbonates, copolycarbonate esters, polyethers, polyetherketones, polyvinylidene fluoride, polybenzimidazoles, polybenzoxazoles, cellulosic derivatives, polyazoaromatics, poly(2,6-dimethylphenylene oxide), polyarylene oxide, polyureas, polyurethanes, polyhydrazides, polyazomethines, cellulose acetates, cellulose nitrates, ethyl cellulose, brominated poly(xylylene oxide), sulfonated poly(xylylene oxide), polyquinoxaline, polyamideimides, polyamide esters, blends thereof, copolymers thereof, substituted materials thereof and the like. This should not be considered limiting since any material which can be fabricated into an anisotropic substrate **membrane** may find utility as the substrate layer of the present invention. Preferred materials for the substrate layer include polysulfone, polyethersulfone, polyetherimide, polyimide and polyamide compositions.

#### **Brief Summary Text - BSTX (30):**

For the purpose of illustrating the invention, we exemplify forming multicomponent **membranes** with two components, that is, a gas separating component and a substrate component. This should not be considered limiting, however, since the multicomponent **membranes** of the present invention may incorporate more than two component layers. The additional layers may function as gas separating layers, structural layers, substrate layers, layers which reduce environmental concerns, or combinations thereof. These additional layers may contain the materials employed in the gas separating layer and the substrate layer.

#### **Brief Summary Text - BSTX (31):**

The materials of each layer should be sufficiently compatible to ensure integrity of the **composite membrane** during processing or when employed in fluid separations such as gas separations.

#### **Brief Summary Text - BSTX (33):**

Multicomponent gas separation membranes of the present invention may be in the form of various shapes such as flat membranes or hollow fiber membranes. The membrane is preferably in the form of a hollow fiber due to the surface area advantages available. The flat film membranes may be prepared through coextrusion of the polymer solutions for the separating and support layers to form a nascent multilayer membrane. The nascent multilayer membrane is optionally dried under specified conditions and then precipitated in a coagulating bath that is a non-solvent for the film forming polymer but is a solvent of the polymer solvent. Coextrusion may be performed by use of well known multiple slit dies. For example, a bicomponent film membrane can be coextruded through a two-slit die. The nascent bicomponent film membrane can be supported on a plate, continuous roller, or fabric backing. Such a nascent bicomponent film can be optionally dried at from 10.degree. C. to 200.degree. C., preferably 25.degree. C. to 100.degree. C., for 0.01 to 10 minutes, preferably for 0.05 to 1.0 minutes, by passing the nascent bicomponent film through an oven. The nascent bicomponent film is then precipitated in the coagulating bath.

#### **Brief Summary Text - BSTX (34):**

Multicomponent hollow fiber membranes in the form of hollow fibers may be formed by coextrusion of the support polymer and separating polymer solutions. For example, polymer solutions for the layers may be coextruded through a multiple channel spinneret while maintaining a gas pressure or a bore fluid in the nascent hollow fiber bore to maintain the fiber's structural integrity. Such multiple channel spinnerets have been described in the prior art for use in melt extrusion of multicomponent fibers.

#### **Brief Summary Text - BSTX (35):**

The nascent coextruded hollow fiber membrane optionally may be dried by passing the nascent fiber through an air gap of from 0.1 cm to 6 m, preferably from 0.1 cm to 20 cm, at a temperature of from 10.degree. C. to 250.degree. C., preferably from 20.degree. C. to 100.degree. C., for a time dependent on the coextrusion rate and the fiber takeup speed, generally between 10.sup.-6 to 5 minutes, preferably between 0.001 to 1 minute. The nascent fiber is then drawn into a coagulating bath. The thus formed multicomponent hollow fiber membranes are wound onto a drum or other suitable collection device.

#### **Brief Summary Text - BSTX (36):**

During fabrication of the hollow fiber membranes, the separating layer is preferably formed on the outside surface of the fiber to maximize the membrane surface area exposed to the gas. However, the separating layer also may be formed as the inner layer of the fiber. The multicomponent hollow fiber membrane of the present invention may have an outside diameter of about 75 to 1,000 microns, preferably 100 to 350 microns,

and a wall thickness of about 25 to 300 microns, preferably 25 to 75 microns. Preferably the diameter of the bore of the fiber is about one-half to three-quarters of the outside diameter of the fiber.

#### Brief Summary Text - BSTX (37):

The porosity of the resultant membrane is sufficient so that the void volume of the membrane is within the range of 10 to 90 percent, preferably about 30 to 70 percent, based on the volume contained within the gross dimensions of the overall multicomponent membrane.

#### Brief Summary Text - BSTX (38):

Coextrusion, and the apparatus and processes therein, of polymers is well known in the art. Use of solution coextrusion techniques as in the present invention for the fabrication of multicomponent gas separation membranes, however, is novel and surprising. The optional drying step and the coagulation processes described above also are well known in the prior art for manufacture of monolithic asymmetric membranes. The application of such processes for the fabrication of multicomponent membranes, however, is surprising and novel.

#### Brief Summary Text - BSTX (39):

In order to select suitable materials for use as the separating layer and/or substrate layer of the multicomponent membranes, a two step process for the fabrication of bicomponent membranes may be employed. This process entails casting a polymer solution onto a glass plate at a specified temperature with a casting knife, for example, a knife gap of 15 mils (3.8.times.10.sup.-4 m) to form a nascent substrate layer. After drying on the plate for a specified time, the separating layer polymer solution is cast on top of the substrate layer through use of a larger knife gap, for example, a knife gap of 20 mils (5.1.times.10.sup.-4 m). After drying for a specified time and temperature, the resultant nascent bicomponent film is coagulated in a bath that is a nonsolvent for the polymers but which is a solvent for the solvents of the polymeric solutions employed to form the separating and substrate layers.

#### Brief Summary Text - BSTX (40):

Selection of the polymer solutions for use in the production of the various layers of the multicomponent membrane may be made depending on, for example, the solubility characteristics of the polymer and the desired end use of the layer. Typically, such polymer solutions are similar to those described in the prior art for asymmetric membranes. The amount of polymer in each solution independently may vary from about 1 to 60 weight percent, preferably 15 to 35 weight percent.

### **Brief Summary Text - BSTX (42):**

Mixtures of solvents also may be used in the polymer solutions employed to form the layers of the **membrane**. The specific mixture of solvents may vary depending on the solubility parameters of the polymer and the desired use of the layer. For example, two or more solvents may be used which vary in volatility or solvation power. Specific examples of polymer solutions which include mixtures of solvents for use with a variety of polymeric materials are exemplified herein.

### **Brief Summary Text - BSTX (43):**

The solvent mixture also may contain additional components such as polymer swelling agents, and nonsolvent components. These added components may be useful, for example, to achieve a desired anisotropy in a layer by moving the polymer solution closer to its point of incipient gelation. These additional components may be characterized as extractable or nonextractable in the coagulation bath. Extractable components, that is, materials which are extractable in an aqueous-based coagulation bath, may be useful, for example, as pore formers in a layer. Examples of extractable components include inorganic salts, and polymers such as polyvinyl pyrrolidone. Nonextractable components may find utility as, for example, **membrane** permeation modifiers. Nonextractable materials vary in composition dependent on the end use desired for the layer and the composition of the polymer, solvent mixture and coagulation bath. Examples of the additional components which may be employed include, for example, discrete monomeric materials which are insoluble in the composition of the coagulation bath, polymerizable materials such as moisture-curable siloxanes, and compatible or non-compatible polymers. The foregoing examples of additional components are merely illustrative and should not be considered limiting.

### **Brief Summary Text - BSTX (44):**

Suitable coagulation baths for the nascent multicomponent **membranes** vary depending on the composition of the polymer solutions employed and the results desired. Generally, the coagulation bath is miscible with the solvent of the solvent mixture, but is a non solvent for the polymers of each layer. However, the coagulation bath may be varied to achieve desired properties in the layer. This may be desirable depending on the solubility parameters of the separating layer polymer, or when specialized **membrane** configurations are desired. For example, the solvent of the separating layer polymer solution may be immiscible in the coagulation bath whereas the solvent of the substrate layer polymer solution may be miscible in the coagulation bath. A coagulation bath therefore may be a multicomponent mixture of water and an organic solvent that is miscible with water and the solvent to be removed from the polymer. The temperature and composition of the bath also may be controlled to affect the extent and rate of coagulation.

### **Brief Summary Text - BSTX (45):**

The Nascent multicomponent membranes can be dried by air drying or other prior art processes. For example, water-wet monolithic asymmetric hollow fiber membranes can be dehydrated by the methods shown in U.S. Pat. Nos. 4,080,743, 4,080,744, 4,120,098, and EPO-219,878.

### **Brief Summary Text - BSTX (46):**

A surprising advantage provided by the present invention is its ability to produce multicomponent membranes of a wide range of compositions and configurations. In the simplest case, the invention can produce bicomponent membranes of a separating layer and a porous substrate layer. The separating layer may be dense or asymmetric. In addition, the present invention offers the advantage of forming separating materials which are otherwise impossible or very difficult to fabricate by prior art techniques into commercially useful membranes. The present invention also surprisingly enables the use of other membrane materials which have not been easily fabricated into useful commercial membranes due to solubility, solution viscosity or other rheological problems.

### **Brief Summary Text - BSTX (47):**

The fabrication processes employed to form the multicomponent membranes of the present invention depend on the major component of the membrane. For example, in manufacture of bicomponent hollow fiber membranes, selection of the spinning parameters depends on the spinnability of the substrate layer solution. This means that bicomponent membranes formed by the present invention readily can be spun essentially under the same conditions as the underlying substrate layer. However, the preferred spinning conditions are selected to optimize the morphology of the separating layer.

### **Brief Summary Text - BSTX (48):**

The multicomponent fiber membranes formed in the present invention possess the superior gas separation properties of the separating layer while maintaining the ease of fabrication of the substrate layer. This ease of fabrication allows for simplified membrane production. For example, one can start by spinning the bicomponent hollow fiber membranes under conditions already established for spinning of the substrate layer. Process modifications then may be made to provide the desired combination of properties for the multicomponent membrane.

### **Brief Summary Text - BSTX (49):**

Another surprising benefit of the present invention is the improved adhesion achieved between the layers of the membrane. A major drawback of prior art composite membranes has been delamination of the dense separating layer from the porous support under end use operating conditions. This shortcoming has been overcome, in part, in the prior art through addition of adhesion promoters between the separating and support layers. This, however, complicates fabrication of these membranes. Surprisingly, the material layers of the present multicomponent membranes do not require the use of adhesion promoters and do not delaminate under end use conditions.

#### **Brief Summary Text - BSTX (50):**

The novel membranes of the invention have use in a wide variety of gas separations. For example, the membranes of the present invention are useful for the separation of oxygen from air to provide enriched oxygen to provide enhanced combustion, and for the separation of nitrogen from air to provide inerting systems; in recovery of hydrogen from hydrocarbon gas in refinery and ammonia plants; separation of carbon monoxide from hydrogen in syngas systems; for separation of nitrogen from ammonia; and separation of carbon dioxide or hydrogen sulfide from hydrocarbons.

#### **Brief Summary Text - BSTX (51):**

The novel multicomponent membranes of the present invention, however, are not limited to use in gas separations. Generally, all known membrane separations can benefit from utilizing the novel membranes described herein. For example, the membranes may find use in reverse osmosis, microfiltration, ultra-filtration or other separations such as bioseparations that require affinity of certain components in a complex mixture with the membrane to effect efficient separations. Materials with the required affinity generally are not easily manufactured into useful membranes. The current invention, however, enables efficient fabrication of such membranes.

#### **Detailed Description Text - DETX (1):**

Without further elaboration, it is believed that one skilled in the art can, using the preceding description, utilize the present invention to its fullest extent. The following preferred specific embodiments are, therefore, to be construed as merely illustrative, and not limitative of the remainder of the disclosure in any way whatsoever. In the following examples, all temperatures are set forth uncorrected in degrees Celsius; unless otherwise indicated, all parts and percentages are by weight. All hollow fiber membranes are tested by flowing the feed gas along the exterior of the fiber.

#### **Detailed Description Text - DETX (5):**

Films of the polyamide prepared above are cast from a 15% polymer solution (based on weight) in N,N-dimethylacetamide onto a glass plate treated with Du Pont Teflon.RTM. dry lubricant at 90.degree. C.+2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) (38.4.times.10.sup.-5 m) knife gap. Du Pont Teflon.RTM. dry lubricant contains a fluorocarbon telomer which reduces the adhesion of the membrane to the glass plate. After drying on the plate at 90.degree. C.+2..degree. C. for 0.25 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 200.degree. C. for 48 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (9):

A centiBarrer s the number of cubic centimeters of gas passed by the membrane at standard temperature and pressure multiplied by the thickness of the membrane in centimeters multiplied by 10.sup.-12 divided by the product of the permeating area of the membrane in square centimeters, the time in seconds times for permeation and the partial pressure difference across the membrane in centimeters of Hg, that is,  
##EQU1## A hollow-fiber composite membrane is prepared from polyether sulfone as the first substrate layer and the above polyamide as the second separating layer. A solution is prepared of 37.5% (weight) VICTREX 600P polyether sulfone (ICI corporation), 15% (weight) polyvinylpyrrolidone (average MW: 10,000, AIDRICH) and 47.5% (weight) DMAc as the solvent. A solution of 20 weight % of the polyamide, 6% (weight) lithium nitrate, 74% DMAc as the solvent is prepared. A third solution of 80% (volume) of DMAc in 20% water is prepared as the bore solution. The hollow fiber spinneret consisted of a needle with dimensions of 16 mils (4.1.times.10.sup.-4 m OD and 10 mils (2.5.times.10.sup.-4 m) ID inserted in an annulus with dimensions of outer diameter of 33 mils (8.4.times.10.sup.-4 m) and inner diameter of 16 mils (4.1.times.10.sup.-4 m). The spinneret temperature is maintained at 91.degree. C. The first substrate polymer solution is extruded at a rate of 263 cc/hr through the annulus. The bore of the fiber is maintained by means of supply of the DMAc solution into the needle at a rate of 60 cc/hr. The second separating layer I0 polymer solution is simultaneously applied at a rate of 32 cc/hr over the first substrate polymer solution using the mesa metering technique described in U.S. Pat. No.2,861,319.

#### Detailed Description Text - DETX (11):

The resulting bicomponent fiber membrane contains about 5% by weight of the polyamide separating layer is treated as taught in U.S. Pat. No. 4,230,463 to seal any defects in the polyamide dense separating layer. Treatment involves contacting the outer surfaces of the fiber with a 5.0% (weight) SYLGARD.RTM. 184 solution in FREON.RTM. 113 (1,1,2-trichloro-1,2,2-trifluoroethane), decanting the solution and

drying the fiber in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. SYLGARD.RTM. 184 (Dow Corning Corporation) is an elastomeric silicone material which thermally cures to a crosslinked silicone material.

#### **Detailed Description Text - DETX (28):**

The foregoing example demonstrates the invention herein. As shown above, a multicomponent, hollow fiber gas separation membrane can be prepared in essentially one step. The multicomponent hollow fiber membrane that is formed combines a gas separating layer, prepared from the separating polymer solution, on the outside surface of an anisotropic substrate membrane prepared from the substrate polymer solution. Although the separating polymer and the substrate polymer may differ compositionally, the multicomponent hollow fiber membrane does not suffer from delamination problems often encountered in the prior art membranes.

#### **Detailed Description Text - DETX (29):**

The foregoing example also illustrates another aspect of the present invention wherein, the separating polymer, although it is the minor component of the membrane, compositionally incorporates the dense gas-separating layer. This is demonstrated by comparing the relative gas separation properties of the separating polymer and the substrate polymer components versus the gas separation properties of the final multicomponent membrane. As shown above, the separating polymer component has a relatively high O<sub>sub.2</sub> / N<sub>sub.2</sub> selectivity of 6.6 whereas the substrate polymer component has a substantially lower O<sub>sub.2</sub> / N<sub>sub.2</sub> selectivity. Surprisingly, the O<sub>sub.2</sub> / N<sub>sub.2</sub> selectivity of final multicomponent membrane more closely approximates the selectivity of the outer polymer than the selectivity of the substrate polymer layer.

#### **Detailed Description Text - DETX (30):**

The foregoing example also illustrates the variety of gas separations, such as hydrogen separations from hydrocarbons, helium separations, air separations and carbon dioxide separations from hydrocarbon streams, in which the present multicomponent membranes find utility.

#### **Detailed Description Text - DETX (32):**

To a stirred solution of 1,4-bis(4-aminophenoxy)biphenyl ##STR17## (372.8 g, 1 mol) in N,N-dimethylacetamide (2600 ml) is dropwise added melted isophthaloyl dichloride (204.0 g, 1.005 mol) under an inert atmosphere. The reaction temperature is maintained at under 52.degree. C. by control of the addition rate. The resulting very viscous solution is stirred for 4 hours at 50.degree. C. and then lithium hydroxide (88.14 g, 3.7 mol) is

added. The resulting reaction mixture is allowed to cool to room temperature and stirred overnight. The reaction solution is diluted with N-methylpyrrolidone and precipitated in water. The resulting solid is collected and washed twice with water and twice with methanol. After air -drying overnight, the solid is dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours and at 250.degree. C. for 4 hours to yield 506.7 g product.

#### Detailed Description Text - DETX (33):

The polyamide prepared above is found to be soluble in dimethylsulfoxide, m-cresol, N,N-dimethylacetamide and N-methylpyrrolidone. Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+-.2.degree. C. with a 15-mil (38.4.times.10.sup.-5 m) knife gap. After drying on the plate at 100.degree. C..+-.2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (34):

Multicomponent membranes are prepared from a dense separating layer of the polyamide prepared above on top of a substrate of VICTREX 600P polyether sulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000, based on polymer weight) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C..+-.3.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polyamide prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the polyethersulfone at 100.degree. C..+-.3.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+-.3.degree. C. for the time noted below, the membrane layers are co-coagulated in a water bath at 27.degree. C..+-.1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the layers.

#### Detailed Description Text - DETX (35):

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit excellent adhesion between the

component layers. The only distinction between the layers is coloration. The top polyamide layer is light tan while the polyethersulfone substrate layer is white.

#### **Detailed Description Text - DETX (36):**

The membrane fabrication procedure employed above demonstrates the applicability of the simplified sequential casting process for the rapid assessment of the utility of materials for multicomponent membranes.

#### **Detailed Description Text - DETX (42):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyether sulfone (a product of ICI). A 25% VICTREX polyether sulfone solution (based on a weight) with 7.5% polyvinylpyrrolidone (M.W. 10,000, based on weight) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the polyethersulfone substrate at 100.degree. C. with a 20-mil knife gap. After drying at 100.degree. C..+- .3.degree. C. for the time noted below, the membranes are coagulated in a water bath at 27.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (43):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit excellent adhesion between the component layers.

#### **Detailed Description Text - DETX (44):**

The membrane fabrication procedure shown above demonstrates the applicability of the materials described therein for gas separation membranes.

#### **Detailed Description Text - DETX (53):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 85.degree. C..-+.2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) (38.4.times.10.sup.-5 m) knife gap. After drying on the plate at 85.degree. C..-+.2.degree. C. for 20 minutes, the films are further dried in a vacuum oven at 20 inches

(0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (57):**

A separating polymer solution is prepared with 25% (weight) solids of the polyimide prepared as above in N,N-dimethylacetamide. A substrate polymer solution is prepared with 37.5% (weight) solids VICTREX 600P polyether sulfone and 15.0% polyvinylpyrrolidone (M.W.=10,000) in N,N-dimethylacetamide. Hollow fiber **membranes** are prepared by extruding the above polymer solutions through a hollow fiber spinneret as described in Example 1. The separating polymer solution is extruded at a rate of 48 cc/hour and the substrate solution is extruded at a rate of 140 cc/hour. A bore fluid of a solution of 80% (volume) N,N-dimethylacetamide in water is injected into the fiber bore at a rate of 72 cc/hour. The spinneret temperature is 60.degree. C. The spun bicomponent fiber is passed through an air gap length of 8.0 cm at room temperature into an aqueous coagulation bath at 23.degree. C. The fiber is wound up on a drum at the rate of 34 meters per minute. The fiber is further washed in water and then allowed to air dry.

#### **Detailed Description Text - DETX (58):**

The fiber **membrane** is tested for mixed gas oxygen/nitrogen (21/79, mole) permeabilities at 100 psig (689 kPa), 25.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (62):**

A bicomponent fiber **membrane** is prepared as in Example 5 except the aqueous coagulation bath temperature is 36.degree. C. The fiber is then treated as in Example 5.

#### **Detailed Description Text - DETX (63):**

The fiber **membrane** is tested for mixed gas oxygen/nitrogen (21/79, mole) permeabilities at 100 psig (689 kPa), 25.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (67):**

A bicomponent fiber **membrane** is prepared as in Example 5 except the aqueous coagulation bath temperature is 15.degree. C. and the fiber is wound up on the drum at a rate of 35 meters per minute. The fiber is then treated as in Example 5.

#### **Detailed Description Text - DETX (72):**

A bicomponent fiber **membrane** is prepared as in Example 5 except the separating polymer solution is extruded at the rate of 24 cc/hour and the bore fluid is injected at a rate of 68 cc/hour. Further, the water-wet fiber is washed for 2 hours in methanol and then washed in pentane for 2 hours. The fiber then is allowed to air dry.

#### **Detailed Description Text - DETX (77):**

A bicomponent fiber **membrane** is prepared as in Example 5 except for the following changes. The separating polymer solution is extruded at a rate of 24 cc/hour and the bore fluid is injected at a rate of 68 cc/hour. The aqueous coagulation bath temperature is 14.degree. C. Further, the water-wet fiber is washed for 2 hours in methanol and then washed for 2 hours in pentane. The fiber is then allowed to air dry.

#### **Detailed Description Text - DETX (87):**

Bicomponent fiber **membranes** are prepared as in Example 10 except the separating polymer solution is extruded at a rate of 15 cc/hour and the aqueous coagulation bath temperature is 6.degree. C. The fiber is treated as in Example 9.

#### **Detailed Description Text - DETX (97):**

Bicomponent fiber **membranes** are prepared as in Example 12 except the separating polymer solution is extruded at a rate of 20 cc/hour. The fiber is then treated as in Example 12.

#### **Detailed Description Text - DETX (112):**

A bicomponent fiber **membrane** is prepared as in Example 14 with the following changes. The separating polymer solution is extruded at a rate of 12 cc/hour. The spinneret temperature is 75.degree. C. The spun bicomponent fiber is passed through an air gap length of 7.0 cm at room temperature into the previous coagulation bath and wound onto a drum at the rate of 20 meters per minute. The fiber is treated as before in Example 14.

#### **Detailed Description Text - DETX (117):**

A bicomponent fiber **membrane** is prepared as in Example 14 with the following changes. The separating polymer solution is extruded at a rate of 12 cc/hour. The spinneret temperature is 71.degree. C. The spun bicomponent fiber is passed through an air gap length of 8.0 cm at room temperature into an aqueous coagulation bath at 25.degree. C. The fiber is wound up on a drum at the rate of 30 meters per minute. The fiber is further washed with water and then allowed to air dry.

### **Detailed Description Text - DETX (122):**

Multicomponent membranes are prepared from the polyimide prepared in Example 14 on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyether sulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 110.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polyimide prepared in Example 14 in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-5 m) gap. After drying at 100.degree..+.3.degree. C. for the time noted below, the membranes are coagulated in a water bath at 27.degree. C.+.1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute, and 1.00 minute, as described above. The water-wet membranes exhibit adhesion between the layers which ranges from poor to good.

### **Detailed Description Text - DETX (123):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit poor to moderate adhesion between the component layers. The dry membranes curled slightly and the layers can be pulled apart.

### **Detailed Description Text - DETX (124):**

The membrane prepared above which had a dry time of 1.00 minute is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported below:

### **Detailed Description Text - DETX (127):**

This example demonstrates the importance in matching of the properties of the materials employed to form the present multicomponent membranes. The poor to moderate adhesion found in this example is possibly due to the greater hydrophilicity of the polyimide material which forms the separating layer over the polyether sulfone substrate material. Greater adhesion of this polyimide separating material is found when the substrate material is matched more closely as in Examples 14, 15, and 16.

### **Detailed Description Text - DETX (129):**

Bicomponent membranes are prepared from ULTEM.RTM. 1000 polyetherimide (a commercial product of G. E. Corporation) on top of VICTREX 600P polyethersulfone. ULTEM.RTM. 1000 is believed to have the structure shown below: ##STR21##

#### Detailed Description Text - DETX (130):

A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. for 0.5 minutes, a 22% ULTEM 1000 polyetherimide solution (weight) in N-methylpyrrolidone is cast on top of the above nascent film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. for the time noted in Table 1, the membranes are coagulated in a water bath at 19.C. The water-wet membranes exhibit good adhesion between the layers.

#### Detailed Description Text - DETX (131):

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

#### Detailed Description Text - DETX (132):

The bicomponent membranes prepared as above as treated as taught in U.S. Pat. No. 4,230,463 to seal defects in the polyetherimide dense separating layer. This involves contacting the membrane with a 5.0% (weight) SYLGARD 184 (available from Dow Corning Corp.) solution in cyclohexane, removing the membrane from the solution and drying the membrane in a vacuum oven (20 inches mercury) at 55.degree. C..+.5.degree. C. overnight.

#### Detailed Description Text - DETX (133):

The bicomponent membranes, treated as above, are tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported in Table 1.

#### Detailed Description Text - DETX (135):

Bicomponent membranes are prepared from ULTEM 1000 polyetherimide (a commercial product of G. E. Corporation) on top of VICTREX 600P polyethersulfone. A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5%

polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate at 100.degree. C. for 0.5 minutes, a 24% ULTEM 1000 polyetherimide (weight) solution in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. for 0.5 minutes, the membranes are coagulated in a water bath at 13.degree. C. The water wet membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (136):**

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours, and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (137):**

The bicomponent membranes prepared as above are treated as taught in U.S. Pat. No. 4,230,463 to seal defects in the polyetherimide dense separating layer. This involves contacting the membrane with a 5.0% (weight) SYLGARD 184 solution in cyclohexane, removing the membrane from the solution and drying the membrane in a vacuum oven at 20 inches (0.51 m) mercury and 55.degree. C. .+- .5.degree. C. overnight.

#### **Detailed Description Text - DETX (138):**

A bicomponent membrane treated as above is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (141):**

This bicomponent membrane is further tested for mixed gas oxygen/ nitrogen (21/79, mole) permeabilities at 100 psig (689 kPa), 23.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (146):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast

on top of the above film at 100.degree. C. with a 20-mil knife gap. After drying at 100.degree. C. for 0.05 minutes, the membranes are coagulated in a water bath at 13.degree. C. The water-wet membranes exhibit good adhesion between the layers.

#### Detailed Description Text - DETX (147):

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

#### Detailed Description Text - DETX (148):

The bicomponent membranes prepared as above are treated as taught in U.S. Pat. No. 4,230,463 to seal defects in the polyamide dense separating layer. This involves contacting the membrane with 5.0% (weight) SYLGARD 184 solution in cyclohexane, removing the membrane from the solution and drying the membrane in a vacuum oven at 20 inches (0.51 m) mercury and 55.degree. C..+- .5.degree. C. overnight.

#### Detailed Description Text - DETX (149):

A membrane treated as above is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported below:

#### Detailed Description Text - DETX (154):

Films of the polymer prepared above are cast from 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (155):

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5

minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above with 6.8% lithium nitrate in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. .+- .3.degree. C. for 0.50 minute, the membranes are coagulated in a water bath at 27.degree. C..+- .1.degree. C. All water-wet membranes exhibit very good adhesion between the layers.

#### **Detailed Description Text - DETX (156):**

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (157):**

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into gas separation membranes.

#### **Detailed Description Text - DETX (160):**

Films of the polymer prepared above are cast from 10% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 85.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 85.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (162):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above with 6.8% lithium nitrate in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. .+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 15.degree. C..+- .1.degree. C. Two membranes are prepared

with dry times of 0.05 minute and 1.00 minute, as described above. All water-wet **membranes** exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (163):**

The resulting bicomponent **membranes** are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The **membranes** are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent **membranes** exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (164):**

The procedure employed in this example demonstrates the applicability of the materials described therein for fabrication into gas separation **membranes**.

#### **Detailed Description Text - DETX (167):**

Films of the polymer prepared above are cast from 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After **drying** on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (168):**

Multicomponent **membranes** are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After **drying** on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above with 6.8% (weight, based on polymer) lithium nitrate in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After **drying** at 100.degree. C..+- .3.degree. C. for the times noted below, the **membranes** are coagulated in a water bath at 23.degree. C..+- .2.degree. C. Three **membranes** are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet **membranes** exhibit excellent adhesion between the layers.

### **Detailed Description Text - DETX (169):**

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

### **Detailed Description Text - DETX (170):**

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into gas separation membranes.

### **Detailed Description Text - DETX (173):**

Films of the polymer prepared above are cast from 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) (38.4.times.10.sup.-5 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

### **Detailed Description Text - DETX (174):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 27.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute, and 1.00 minute, as described above. All water-wet membranes exhibit good adhesion between the layers.

### **Detailed Description Text - DETX (175):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a

vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (176):**

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into gas separation membranes.

#### **Detailed Description Text - DETX (179):**

Films of the polymer prepared above are cast from 10% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (180):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above with 6.8% (weight) lithium nitrate in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below the membranes are coagulated in a water bath at 26.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute, and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (181):**

The resulting bicomponent membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The dry bicomponent membranes exhibit good adhesion between the layers.

### **Detailed Description Text - DETX (182):**

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into such gas separation membranes.

### **Detailed Description Text - DETX (185):**

Films of the polymer prepared above are cast from 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLO.N.RTM. dry lubricant at 100.degree. C..+-2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) (38.4.times.10.sup.-5 m) knife gap. After drying on the plate at 100.degree. C..+-2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

### **Detailed Description Text - DETX (186):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 97.5.degree. C..+-3.degree. C. After drying on the plate for 0.5 minutes at 97.5.degree. C..+-3.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 97.5.degree. C..+-3.degree. C. with a 20-mil knife gap. After drying at 97.5.degree. C..+-3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 27.degree. C..+-1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute, and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the layers.

### **Detailed Description Text - DETX (187):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.C for 4 hours. All dry membranes exhibit excellent adhesion between the layers.

### **Detailed Description Text - DETX (188):**

The bicomponent membrane which is dried 0.5 minutes is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported below:

### **Detailed Description Text - DETX (191):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

### **Detailed Description Text - DETX (195):**

dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C, for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

### **Detailed Description Text - DETX (199):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyvinylpyrrolidone (based on weight) in 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. for the times noted in Table 2, the membranes are coagulated in a water bath at 25.degree. C..+- .1.degree. C. All membranes exhibit excellent adhesion between the layers.

### **Detailed Description Text - DETX (200):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit excellent adhesion between layers.

### **Detailed Description Text - DETX (201):**

The membranes are tested for pure gas helium and nitrogen permeabilities at 100 psig (689kPa), 24.degree. C. The results are reported in Table 2.

### **Detailed Description Text - DETX (202):**

The bicomponent membranes prepared as above are treated as taught in U.S. Pat. No. 4,230,463 to seal defects in the polyimide dense separating layer. This involves

contacting the membrane with a 5.0% (weight) SYLGARD 184 solution in cyclohexane, removing the membrane from the solution and drying the membrane in a vacuum oven (20 inches mercury at 55.degree. C..+- .5.degree. C. overnight.

#### Detailed Description Text - DETX (203):

The treated bicomponent membrane of Example 31 is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 24.degree. C. The treated bicomponent membrane of Example 32 is tested for mixed gas oxygen/nitrogen (21/79, mole) permeabilities at 100 psig (689 kPa), 23.degree. C. The treated bicomponent membrane of Example 35 is tested for pure gas carbon dioxide permeability at 100 psig (689 kPa), 25.degree. C. The results are reported in Table 3.

#### Detailed Description Text - DETX (204):

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into gas separation membranes.

#### Detailed Description Text - DETX (207):

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (208):

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 25.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute 0.50 minute, and 1.00 minute, as described above. All membranes exhibit good adhesion between the layers.

### **Detailed Description Text - DETX (209):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight at 100.degree. C. for 4 hours. All dry membranes exhibit good adhesion between the component layers.

### **Detailed Description Text - DETX (210):**

The procedure of this example demonstrates the applicability of the materials described therein for fabrication into gas separation membranes.

### **Detailed Description Text - DETX (212):**

A stirred solution of 4,4'-[1,4-phenylenebis(1-methylethyldene)]bisaniline (68.8 g, 0.20 mol), 5,5'-[2,2,2-trifluoro-1-(trifluoromethyl) ethylidene]-bis-1,3-isobenzofurandione (97.2 g, 0.2025 mol) and N-methylpyrrolidone (900 ml) is slowly heated to reflux under an inert atmosphere while collecting distillates. After heating at reflux for 4 hours, a total of 346 ml distillate is collected. The viscous reaction solution is cooled to room temperature, diluted with N-methylpyrrolidone, and precipitated in water. The resulting solid is collected and washed twice with methanol. After air -drying overnight, the solid is dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 3 hours and at 210.degree. C. for 4 hours to yield 139.4 g of polymer product.

### **Detailed Description Text - DETX (213):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

### **Detailed Description Text - DETX (214):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinyl pyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil

(3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 28.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute, and 1.00 minute, as described above. All membranes exhibit good adhesion between the layers.

#### Detailed Description Text - DETX (215):

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM.113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight at 100.degree. C. for 4 hours. All dry membranes exhibit good adhesion between the component layers.

#### Detailed Description Text - DETX (216):

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### Detailed Description Text - DETX (222):

The above solutions are coextruded through a composite fiber spinneret having fiber channel dimensions as set forth in Example 4. The separating polymer solution is extruded at a rate of 16 cm.sup.3 /hr, and the substrate polymer solution is extruded at a rate of 140 cm.sup.3 /hr. A solution of 90% by volume of N-methyl-2-pyrrolidone in water is injected into the bore of the fiber at a rate of 60 cm.sup.3 /hr while the spinneret is maintained at 85.degree. C. The spun bicomponent fiber is passed through an air-gap of 2.5 cm at room temperature into a water coagulation bath at 27.degree. C. The composite fiber then is wound on a drum at a rate of 100 meters/min. The composite fiber then is washed with 50.degree. C. water for about 12 hours and then solvent exchange dehydrate by using methanol and F-113 as described in U.S. Pat. Nos. 4,080,743; 4,080,744; and 4,120,098. The composite fiber is tested for mixed gas O.sub.2 /N.sub.2 (21/79, mole) at 100 psi at 25.degree. C. The fibers exhibit the following separation performance:

#### Detailed Description Text - DETX (225):

The composite fibers as described above then are treated to seal defects in the separating layer as taught in U.S. Pat. No. 4,230,463 which is incorporated herein by reference. The treatment involves contacting the outer surfaces of the fibers with 2.5% by

weight solution of a polysiloxane of the tradename of SYLGARD 184, in FREON 113, decanting the solution, and drying the fibers in a vacuum oven at 20 inches mercury overnight. The composite fiber treated as above is retested for mixed gas O.sub.2 /N.sub.2 (21/79 mole) at 100 psi feed from 25.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (230):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (231):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. for the times noted in Table 4, the membranes are coagulated in a water bath at 24.degree. C..+- .1.degree. C. All membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (232):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperatures overnight at 100.degree. C. for 4 hours. All dry membranes exhibit good adhesion between the component layers.

#### **Detailed Description Text - DETX (233):**

The membranes prepared as above are tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 25.degree. C. The results are reported in Table 4.

#### **Detailed Description Text - DETX (237):**

The bicomponent membranes of Examples 43, 44, and 45 prepared as above are treated as taught in U.S. Pat. No. 4,230,463 to seal defects in the polyimide dense separating layer. This involves contacting the membrane with 5.0% (weight) SYLGARD 184 solution in cyclohexane, removing the membrane from said solution and drying the membrane in a vacuum oven at 20 inches (0.51 m) mercury and 55.degree. C..+-..5.degree. C. overnight.

#### **Detailed Description Text - DETX (238):**

The treated bicomponent membrane of Example 43 is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 23.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (241):**

The treated bicomponent membrane of Example 44 is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 23.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (244):**

The treated bicomponent membrane of Example 46 is tested for pure gas helium and nitrogen permeabilities at 100 psig (689 kPa), 23.degree. C. The results are reported below:

#### **Detailed Description Text - DETX (247):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### **Detailed Description Text - DETX (250):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+-..2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+-..2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (251):**

Multicomponent **membranes** are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 0 15-mil (3.8.times.10 m) knife gap at 95.degree. C. After **drying** on the plate for 0.5 minutes at 95.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 95.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After **drying** at 95.degree. C. for four seconds, the **membrane** is coagulated in a water bath at 18.degree. C. The **membrane** exhibits good adhesion between the polymer layers.

#### **Detailed Description Text - DETX (252):**

The resulting **membrane** is washed in water for 24 hours, washed in methanol for 2 hours and

#### **Detailed Description Text - DETX (253):**

in FREON.RTM. 113 for 2 hours. The **membrane** is dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours.

#### **Detailed Description Text - DETX (257):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.4 m) (38.4.times.10 m) knife gap. After **drying** on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (258):**

Multicomponent **membranes** are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.4 m) knife gap at 100.degree. C. After **drying** on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (based on weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil

(5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the time noted below, the membranes are coagulated in a water bath at 27.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the polymer layers.

#### **Detailed Description Text - DETX (259):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit excellent adhesion between layers.

#### **Detailed Description Text - DETX (260):**

The membrane fabrication procedure of this example demonstrates the applicability of the material described therein for gas separation membranes.

#### **Detailed Description Text - DETX (263):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (264):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (based on weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3 C. for the time noted below, the membranes are coagulated in a water bath at 20.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00

minute, as described above. All water-wet membranes exhibit good adhesion between the polymer layers.

#### **Detailed Description Text - DETX (265):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit good adhesion between layers.

#### **Detailed Description Text - DETX (266):**

The membrane fabrication procedure of this example demonstrates the applicability of the material described therein for gas separation membranes.

#### **Detailed Description Text - DETX (269):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (273):**

Multicomponent membranes are prepared from the polymer prepared above on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast onto a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C. for the time noted in Table 6, the membranes are coagulated in a water bath at 21.degree. C. The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours.

#### **Detailed Description Text - DETX (275):**

The **membrane** fabrication procedure of these examples demonstrates the applicability of the material described therein for gas separation **membranes**.

#### **Detailed Description Text - DETX (278):**

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After **drying** on the plate at 100.degree. C..+- .21.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (282):**

Multicomponent **membranes** are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyether sulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 97.5.degree. C..+- .3.0.degree. C. After **drying** on the plate for 15 seconds, a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 97.5.degree. C..+- .3.0.degree. C. with a 20-mil (5.1.times. 10.sup.-4 m) knife gap. After **drying** at 97.5.degree. C..+- .3.0.degree. C. one minute, the **membrane** is coagulated in a water bath at 25.0.degree. C..+- .1.0.degree. C. Good adhesion between the polymer layers is apparent.

#### **Detailed Description Text - DETX (283):**

The resulting **membrane** is washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The **membrane** is dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The **membranes** exhibit good adhesion between the polymer layers.

#### **Detailed Description Text - DETX (284):**

The **membrane** is tested for pure gas helium, nitrogen, and carbon dioxide permeabilities and mixed gas oxygen/nitrogen (21/79, mole) permeabilities at 100 psig (689 kPa), 24.degree. C. The results are reported in Table 7.

#### **Detailed Description Text - DETX (285):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### Detailed Description Text - DETX (288):

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120 C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (289):

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W. 10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 22% polymer solution (based on weight) of the polymer prepared above in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the time noted below, the membranes are coagulated in a water bath at 15.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All membranes exhibit excellent adhesion between the polymer layers.

#### Detailed Description Text - DETX (290):

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit excellent adhesion between the component layers.

#### Detailed Description Text - DETX (291):

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### Detailed Description Text - DETX (294):

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C. .+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### Detailed Description Text - DETX (295):

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above with 6.8% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 25.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All membranes exhibit excellent adhesion between the polymer layers.

#### Detailed Description Text - DETX (296):

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit excellent adhesion between the component layers.

#### Detailed Description Text - DETX (297):

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### Detailed Description Text - DETX (300):

Films of the polymer prepared above are cast from a 15% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 15-mil (3.8.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the

films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (301):**

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 20% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 23.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (302):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit excellent adhesion between the component layers.

#### **Detailed Description Text - DETX (303):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### **Detailed Description Text - DETX (306):**

Films of the polymer prepared above are cast from a 10% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 0-mil (5.1.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches

(0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (307):**

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 0P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 19.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (308):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. All dry membranes exhibit good adhesion between the component layers.

#### **Detailed Description Text - DETX (309):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### **Detailed Description Text - DETX (312):**

Films of the polymer prepared above are cast from a 10% polymer solution (based on weight) in N-methylpyrrolidone onto a glass plate treated with Du Pont TEFLON.RTM. dry lubricant at 100.degree. C..+- .2.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying on the plate at 100.degree. C..+- .2.degree. C. for 0.5 hour, the films are further dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight. The films are stripped off the plate and dried in a vacuum oven at 20 inches (0.51 m) mercury and 120.degree. C. for 4 hours. The films are tough and flexible and can be creased without cracking.

#### **Detailed Description Text - DETX (313):**

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 23.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All membranes exhibit excellent adhesion between the layers.

#### **Detailed Description Text - DETX (314):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit good adhesion between the component layers.

#### **Detailed Description Text - DETX (315):**

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### **Detailed Description Text - DETX (319):**

Multicomponent membranes are prepared from the above polymer on top of VICTREX 600P polyethersulfone (a product of ICI). A 25% VICTREX 600P polyethersulfone solution (based on weight) with 7.5% polyvinylpyrrolidone (M.W.=10,000) in N-methylpyrrolidone is cast on a glass plate with a 15-mil (3.8.times.10.sup.-4 m) knife gap at 100.degree. C. After drying on the plate for 0.5 minutes at 100.degree. C., a 24% polymer solution (based on weight) of the polymer prepared above in a 8.5% lithium nitrate solution (weight) in N-methylpyrrolidone is cast on top of the above film at 100.degree. C. with a 20-mil (5.1.times.10.sup.-4 m) knife gap. After drying at 100.degree. C..+- .3.degree. C. for the times noted below, the membranes are coagulated in a water bath at 17.degree. C..+- .1.degree. C. Three membranes are prepared with dry times of 0.05 minute, 0.50 minute and 1.00 minute, as described above. All water-wet membranes exhibit good adhesion between the layers.

#### **Detailed Description Text - DETX (320):**

The resulting membranes are washed in water for 24 hours, washed in methanol for 2 hours and washed in FREON.RTM. 113 for 2 hours. The membranes are dried in a vacuum oven at 20 inches (0.51 m) mercury and room temperature overnight and at 100.degree. C. for 4 hours. The membranes exhibit good adhesion between the component layers.

#### Detailed Description Text - DETX (321):

The membrane fabrication procedure of this example demonstrates the applicability of the materials described therein for gas separation membranes.

#### Detailed Description Paragraph Table - DETL (1):

<u>Membranes</u>	Example (min)	PHe (GPU)	PHe/PN.sub.2	Dry Time Treated										
				18	0.5	93	36	19	1.0	90	113	20	2.0	22
21	3.0	63	10											

#### Claims Text - CLTX (1):

1. A multicomponent membrane comprising,

#### Claims Text - CLTX (3):

2. The multicomponent membrane of claim 1 wherein said substrate is selected from the group of polysulfones, polyether sulfones, polyetherimide, polyimide, polyamide, polyesters, or mixtures thereof.

#### Claims Text - CLTX (4):

3. The multicomponent membrane of claim 1 wherein Ar is ##STR33## or mixtures thereof.

#### Claims Text - CLTX (5):

4. The membrane of claim 3 wherein --R-- is a mixture of ##STR34##

#### Claims Text - CLTX (6):

5. The membrane of claim 3 wherein --R-- is a mixture of ##STR35##

#### Claims Text - CLTX (7):

6. The multicomponent membrane of claim 1 wherein R is ##STR36##

**Claims Text - CLTX (8):**

7. The multicomponent membrane of claim 1 where R is ##STR37##

**Claims Text - CLTX (9):**

8. The membrane of claim 1 wherein R is ##STR38##

**Claims Text - CLTX (10):**

9. The membrane of claim 1 wherein --R-- is ##STR39##

**Claims Text - CLTX (11):**

10. The membrane of claim 1 wherein --R-- is ##STR40##

**Claims Text - CLTX (12):**

11. The membrane of claim 1 wherein --R-- is ##STR41##

**Claims Text - CLTX (13):**

12. The membrane of claim 1 wherein --R-- is ##STR42##

**Claims Text - CLTX (14):**

13. The membrane of claim 1 wherein --R-- is a mixture of ##STR43##

**Claims Text - CLTX (15):**

14. The membrane of claim 1 wherein --R-- is a mixture of ##STR44##

**Claims Text - CLTX (16):**

15. The membrane of claim 1 wherein --R-- is a mixture of ##STR45##

**Claims Text - CLTX (17):**

16. The membrane of claim 1 wherein --R-- is ##STR46##

**Claims Text - CLTX (18):**

17. The membrane of claim 1 wherein --R-- is a mixture of ##STR47##

**Claims Text - CLTX (19):**

18. The membrane of claim 1 wherein --R-- is ##STR48##

**Claims Text - CLTX (20):**

19. The membrane of claim 1 wherein --R-- is a mixture of ##STR49##

**Claims Text - CLTX (21):**

20. A multicomponent membrane comprising a porous polymeric substrate and a polyimide separating layer for separating gases wherein said polyimide is an aromatic polyimide comprising repeating units of the formula: ##STR50## wherein R and R' are selected from the group ##STR51## where --Z-- is a carbon-carbon single bond, ##STR52## alkylene groups of 1 to 5 carbon atoms, --Ar-- is ##STR53## for mixtures thereof where Z', Z'', Z''' independently are a carbon-carbon single bond, ##STR54## or alkylene groups of 1 to 5 carbon atoms, X, X.sub.1, X.sub.2 and X.sub.3 are independently, hydrogen, alkyl groups of 1 to 5 carbon atoms, alkoxy groups of 1 to 5 carbon atoms, phenyl or groups, --Y, --Y.sub.1, --Y.sub.2, --Y.sub.3, --Y.sub.4, --Y.sub.5, --Y.sub.6, --Y.sub.7, --Y.sub.8, --Y.sub.9, --Y.sub.10, --Y.sub.11, --Y.sub.12, --Y.sub.13, --Y.sub.14, and --Y.sub.15 independently are --X, --X.sub.1, --X.sub.2, --X.sub.3 or halogen, --Ar'-- is ##STR55## or mixtures thereof where Z' has the above-defined meaning, m is 0 to 100 mole percent, n is 0 to 100 mole percent, and (m+n)=100%.

**Claims Text - CLTX (22):**

21. The membrane of claim 20 wherein m is 20 to 100 mole percent and n is 20 to 100 mole percent.

**Claims Text - CLTX (23):**

22. The membrane of claim 20 wherein said polymeric substrate is selected from the group of polysulfones, polyether sulfones, polyetherimide, polyimide, polyamide, polyesters, or mixtures thereof.

**Claims Text - CLTX (24):**

23. The membrane of claim 20 wherein R is ##STR56##

**Claims Text - CLTX (25):**

24. The membrane of claim 20 wherein --Ar-- is a mixture of ##STR57##

**Claims Text - CLTX (26):**

25. The membrane of claim 20 wherein --Ar-- is ##STR58## or mixtures thereof.

**Claims Text - CLTX (27):**

26. The membrane of claim 20 wherein --Ar-- is ##STR59##

**Claims Text - CLTX (28):**

27. The membrane of claim 20 wherein --Ar-- is ##STR60##

**Claims Text - CLTX (29):**

28. The membrane of claim 20 wherein --Ar-- is ##STR61##

**Claims Text - CLTX (30):**

29. The membrane of claim 20 wherein --Ar-- is ##STR62##

**Claims Text - CLTX (31):**

30. The membrane of claim 20 wherein --Ar-- is ##STR63##

**Claims Text - CLTX (32):**

31. The membrane of claim 20 wherein --Ar-- is ##STR64##

**Claims Text - CLTX (33):**

32. The membrane of claim 20 wherein --Ar-- is ##STR65##

**Claims Text - CLTX (34):**

33. The membrane of claim 20 wherein R is ##STR66##

**Claims Text - CLTX (35):**

34. The membrane of claim 33 wherein --Ar-- is a mixture of ##STR67##

**Claims Text - CLTX (36):**

35. The membrane of claim 33 wherein --Ar-- is ##STR68##

**Claims Text - CLTX (37):**

36. A process for manufacture of a multicomponent gas separation membrane, comprising providing a solution of a film forming polymer as a first supporting layer, said film forming polymer of said solution being selected from the group of polysulfones, polyether sulfones, polyetherimides, polyimides, polyamide, copolymers thereof, and blends thereof, applying to a surface of said first supporting layer a second solution of a film forming polymer to provide a separating layer to form a nascent membrane of at least two layers, said film forming polymer of said second solution being selected from the group of polyetherimide, polyimide, polyamide, polyesters, polycarbonates, copolycarbonate esters, polyphenylene oxides, polyamideimides, cellulose acetates, ethyl cellulose and mixtures thereof, coagulating said nascent membrane, and drying said nascent membrane to form a multicomponent gas separation membrane.

**Claims Text - CLTX (39):**

38. The process of claim 37 wherein said coextruding yields a membrane in the form of a hollow fiber having said separating layer on the exterior of said fiber.

**Claims Text - CLTX (40):**

39. The process of claim 38 wherein said separating layer is in the form of an asymmetric membrane.

**Claims Text - CLTX (46):**

45. The process of claim 36 wherein said nascent membrane is dried to remove solvent from said separating layer prior to said coagulating.